PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : D06M 16/00

A1

(11) International Publication Number: WO 89/ 03909

(43) International Publication Date: 5 May 1989 (05.05.89)

(21) International Application Number: PCT/EP88/00971

(22) International Filing Date: 27 October 1988 (27.10.88)

(31) Priority Application Number: 4214/87

(32) Priority Date: 28 October 1987 (28.10.87)

(33) Priority Country: CH

(71) Applicant *(for all designated States except US)*: SCHOELLER HARDTURM AG [CH/CH]; Hardturmstrasse 122, CH-8005 Zurich (CH).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)* : CIAMPI, Luigi [IT/CH]; Türkheimerstrasse 5, CH-4055 Basle (CH). FORSTER, Otto [CH/CH]; Im Sydefädeli 41, CH-8037 Zurich (CH). HAEFELY, Hans, Rudolf [CH/CH]; Kempfhofweg 10, CH-8037 Zurich (CH). KNAUSEDER, Franz [AT/AT]; Oberndorf 306, A-6322 Kirchbiehl (AT).

(74) Agent: D'HAEMER, Jan; Sandoz AG, Patentabteilung, CH-4002 Basle (CH).

(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent), US.

Published
*With international search report.*
*Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: ENZYMATIC TREATMENT OF WOOL

(57) Abstract

The invention relates to a process for the production of wool and animal hairs with a low-in felt or felt-free finish, with a soft woolly handle and special shrink-resistance and strength. In this process, the wool is treated with a protease and is then treated at a temperature of between room temperature and 140°C.

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | |
|---|---|---|---|---|---|
| AT | Austria | FR | France | ML | Mali |
| AU | Australia | GA | Gabon | MR | Mauritania |
| BB | Barbados | GB | United Kingdom | MW | Malawi |
| BE | Belgium | HU | Hungary | NL | Netherlands |
| BG | Bulgaria | IT | Italy | NO | Norway |
| BJ | Benin | JP | Japan | RO | Romania |
| BR | Brazil | KP | Democratic People's Republic of Korea | SD | Sudan |
| CF | Central African Republic | | | SE | Sweden |
| CG | Congo | KR | Republic of Korea | SN | Senegal |
| CH | Switzerland | LI | Liechtenstein | SU | Soviet Union |
| CM | Cameroon | LK | Sri Lanka | TD | Chad |
| DE | Germany, Federal Republic of | LU | Luxembourg | TG | Togo |
| DK | Denmark | MC | Monaco | US | United States of America |
| FI | Finland | MG | Madagascar | | |

ENZYMATIC TREATMENT OF WOOL

The present invention relates to a process for the production of wool and animal hairs with a low-in-felt or felt-free finish and to the wool or animal hairs so obtained.

To obtain felt-free wool has been a problem for many years and many methods including enzymatic treatments have been proposed to solve this problem. A review of such methods has been published by E.P. Frieser in Textil-Praxis, 18 (1963, 03), pages 236-240 and he refers back to articles by W.R. Middlebrook and H. Phillips in J. Soc.Dyers and Colorists, 57 (1941), pages 137-144 and A.N. Davidson and R. Preston in J. Text. Inst. 47 (1956), pages 685-707 (also described in Belgian Patent No. 536 819). Although not always as explicitly stated as in European Patent Application 134 267, the object of these enzymatic treatments was to achieve a complete descaling of the wool, i.e. that the outer surface of the fibres is totally removed and the character of the fibres changed in such a way that the natural aspect of the wool is lost.

The object of the present invention is to produce wool and animal hairs which keep their natural aspect and still have scales, but are low-in--felt or felt-free. This object is achieved by an enzymatic treatment which, in contrast to the known treatments, is superficial and short but effective to obtain a product that can be washed without negative consequences in ordinary household washing machines. A reliable method to differentiate this product from natural wool is the IWS Test Method 31, published by the International Wool Secretariate. Whereas the untreated fibres start to felt at the latest after 3 cycles of the described 7 A washes, the enzymatically treated wool according to the invention can stand at least 5 of these cycles without felting.

Another method to determine whether the wool fibres can be called felt--free is the well known Cubex-Test according to IWS Test Method 185, in which the shrinkage properties of wool are determined by treatment for one hour in cube form in a standardised washing appliance. In this test the wool should have an area shrinkage of < 10 % after a Cubex test lasting at least one hour. By area shrinkage is understood the sum of the % shrinkage in length and of the % shrinkage in width. This corresponds to about 15-20 machine washes at high speed in a domestic washing machine without shrinkage or without significant alteration to the surface and shape.
Furthermore, the yarn strength of the treated wool should, compared with untreated wool, be lost by less than 15 % Rkm and the elongation should deteriorate by less than 20 %.

The invention, therefore, relates to a process for the production of wool or protein containing animal hair, which have (in addition to a soft handle and a natural wool appearance) a low-in-felt or felt-free finish defined by the following properties:

a) an area shrinkage of $\leq$ 10 % after a Cubex test lasting at least one hour or after 5 cycles 7 A according to IWS TM 31,

b) a loss of yarn strength, compared with untreated wool or hair, of less than 15 % Rkm, and

c) an elongation which deteriorates by less than 20 %,

characterised by bringing the wool into contact with a protease, and subsequently treating it at a temperature between room temperature(20°C) and 140°C.

By protease is understood any protein-splitting enzyme. Suitable proteases are enzymes recovered from bacteria, for example esperase, pronase

E, protease P, subtilysin, thermolysin, as well as enzymes from animal or plant origin, for example trypsin, pepsin, pancreatin or bromelain. Mixtures of various enzymes can also be used. These proteases are available commercially. Preferred proteases for the process according to the invention are the animal and vegetable enzymes, especially bromelain.

The effectiveness of the enzyme employed can be increased by adding specific activators such as cystein, dithioerythrol, dithiothreitol or mercaptoethanol. Further additives, such as salts which are known for stabilising enzymes, can also be used, e.g. calcium or zinc chloride. These salts are employed in a quantity which corresponds to the enzyme.

Treatment of the wool or hair with a protease may take place in a long or short bath. Treatment is preferably effected by means of impregnation from a short bath, for example by padding, spraying, coating or printing. The protease may be applied from an aqueous medium or from organic solvent, or also as a paste or foam. The liquor-to-goods ratio is conveniently in the range 1:0.7 to 1:10, preferably 1:1 to 1:5 if treatment is continuous, and in the range 1:10 to 1:40 if treatment is from a long bath.

Application of the protease is preferably effected at a temperature between room temperature and 60°C. The treatment liquor or paste is preferably set at a pH value between 4 and 9, especially 5-7, using a commercial buffer.

The protease is conveniently used in a quantity of 0.1 to 5 %, calculated on the dry weight of the wool. When applied by means of impregnation, the protease is used in a quantity of 0.1 to 2 %, corresponding to an enzyme activity of 400 to 1500 CDU/mg. Preferably a quantity of 0.5 to 1 % is used. When applied from a long bath, the protease is used in a quantity of 1 to 5 %, again calculated on the dry weight of the wool.

Directly after the enzymatic treatment, the wool or hair is either left

to dwell and/or undergoes thermal treatment. The dwelling period may last from a short interim period to several hours, with partial or complete drying of the goods. Depending on the temperature, the thermal treatment may take place for a few minutes up to several hours, optionally until the wool is dry. Saturated steam, super-heated steam, hot air or high frequency (HF) waves may be used for the thermal treatment. When steaming with saturated steam for example, the wool or hair is advantageously left to dwell for between 10 and 30 minutes. In the HF drier, the wool or hair is conveniently treated at about 100-102°C between 10 minutes and 1 hour. The conditions for the dwelling period or the thermal treatment are chosen such that the wool obtained has the desired properties, and preferably such that the enzyme is simultaneously disactivated at the end of the treatment. Any enzyme that is still active can also be disactivated by known methods after treatment.

The wool or hair is then washed and dried, and further processed.

The process according to the invention may be used both for wool and for other protein-containing animal hairs. The fibre material may exist in various stages of processing, e.g. in the form of flocks, tops and roving, yarn, knitted goods, woven goods, non-wovens or felts. The wool may be used for the process according to the invention in the raw or pre-treated state.

In order to attain certain effects and/or to optimise the effect of the protease, it may be convenient to carry out special pre-treatments prior to the enzymatic treatment. Suitable pre-treatments for wool or hair may be for example oxidative treatments, e.g. with hydrogen peroxide, optionally in the presence of a stabiliser, with potassium permanganate, Caro's acid, chlorine or chlorine-containing compounds such as chlorine gas, hypochlorites or organic chlorine carriers, or with ozone, reducing pre-treatments, e.g. with hydrosulphite, a sulphoxylate or sulphide, alkaline treatments, pre-treatments with acids, solvents or enzymes such as lipases, catalases, oxydases or peroxydases, or physical treatments,

for example with various forms of radiation such as HF waves or cold discharges. These pre-treatments are known and are used in part to modify the wool.

After the pre-treatment, the wool or hair is rinsed and dried.

In a preferred feature of the process according to the invention, the wool or hair is chlorinated by oxidation and then treated with a protease.

The oxidative chlorination of the wool or hair is preferably carried out using active chlorine, e.g. in the form of chlorine gas in water or in the form of sodium hypochlorite with hydrochloric acid. This pre-treatment may be carried out by known methods. The wool or hair preferably undergoes mild chlorination. The wool or hair is preferably chlorinated with a quantity of 0,1 to 2 % of active chlorine, calculated on the dry weight of the wool or hair. This treatment advantageously takes place at a pH of 2-3 for 1 to 10 seconds. Chlorination is preferably effected at a temperature of between 10 and 30°C.

After the pre-treatment, in order to attain the desired enzymatic effect, it is advantageous for the wool or hair to be free from residual pre--treatment agents and to have a pH in a neutral range.

After chlorination, the fibre material is treated so as to be free from residual chlorine, and is subsequently or simultaneously neutralised. The chlorine present on the fibre or in the fibre is removed by treatment with a reducing agent, for example sodium bisulphite, sodium sulphite etc. Neutralisation is advantageously carried out with an alkaline compound, for example an alkali metal carbonate.

Depending on the chosen conditions of the process, with or without pre-treatment, the scaly layer of the wool or hair is partly or only slightly changed or activated. As a result of the enzyme treatment,

wool or hair is obtained which has reduced felt behaviour and does not provoke problems during further processing (spinning, bleaching, dyeing) and during usage and washing of the articles made therefrom. The wool which is treated in accordance with the invention has a soft and, which is particularly advantageous, natural woolly handle. When it is chlorinated as tops and is then treated enzymatically as mentioned above, an especially soft wool or hair is produced. The dyeing behaviour of the wool or hair which is treated according to the invention and the fastness properties of the dyed wool or hair are also not adversely affected, on the contrary they are considerably improved.

The following examples illustrate the invention. All percentages are by weight and all temperatures are given in Centigrades.

EXAMPLE 1

Wool tops are padded at 40° with an aqueous liquor which is buffered to pH 6.0 and contains 0.5 % esperase [Bac. lich., obtainable from Novo (Denmark)] calculated on the dry weight of the tops, and then squeezed out to a pick-up of 50 %.

The impregnated tops are subsequently left to dwell for 15 minutes in saturated steam at 102°. After this treatment, the tops are washed out and then dried.

A soft wool which is low in felt and which can be spun with little waste is obtained.

EXAMPLE 2

The process of example 1 is repeated, whereby after padding and squeezing

out, the tops are first of all left for an interim period and then treated for 30 minutes in a HF drier at 100-102°.

EXAMPLE 3

Wool tops are firstly padded for 3 seconds at a temperature of 10-20° on a split padder for tops with chlorine water containing 0.4 % active chlorine. The wool is subsequently rinsed, then treated for 45 seconds with liquor containing 4 g/l sodium carbonate and 1 g/l sodium bisulphite, and washed twice.
After drying, the chlorinated tops undergo enzymatic treatment in accordance with example 1 or 2.

EXAMPLE 4

Wool tops are treated for 60 minutes at 30° with a bath containing, per litre, 15 ml of hydrogen peroxide 40 % by volume and 3 ml of a commercial silicate-free hydrogen peroxide stabiliser, set at a pH of 5.5 - 6.0. The liquor-to-goods ratio is 1:20. The tops are then rinsed and subsequently treated enzymatically according to the process of example 1.

EXAMPLE 6

Wool tops are treated for 5 hours at 45° with a bath containing, per litre, 15 ml of hydrogen peroxide 40 % by volume and 4 g/l of sodium pyrophosphate, set at a pH of 7.5 - 8.5. The liquor-to-goods ratio is 1:20. The wool is subsequently rinsed and then treated enzymatically as described in example 1.

EXAMPLE 7

Wool tops are treated for 60 minutes at 20° with a bath containing 6 % peroxymonosulphuric acid (Caro's acid). The liquor-to-goods ratio is 1:20. 2 % sulphuric acid is subsequently added to the bath, and the wool is treated further with this bath for 30 minutes at 26°. Then, 12 % sodium sulphite is added to the bath, and the wool is further treated for 20 minutes at 30°.
After rinsing, the wool is treated enzymatically according to example 1.

EXAMPLE 8

Wool tops are padded at 30° with liquor containing, per litre, 25 ml of hydrogen peroxide 40 % by volume and 25 g/l of potassium persulphate, set at a pH of 7. The pick-up is 60 %. After leaving at room teperature for 10 hours, the wool is washed out and subsequently treated enzymatically as described in example 1 or 2.

EXAMPLE 9

Wool tops are treated for 6 hours at 40° with a bath containing 0.5 % of a commercial peroxidase and 0.25 mol/l hydrogen peroxide. The liquor-to--goods ratio is 1:25. The wool is subsequently rinsed and then treated with the esperase as in example 1 or 2.

EXAMPLE 10

Wool tops are treated for 6 hours at 40° with a bath containing 0.5 % of a commercial lipase. The liquor-to-goods ratio is 1:20. The wool is subsequently rinsed and then treated with the esperase as in example 1 or 2.

EXAMPLE 11

Wool tops are padded to a pick-up of 50 % with liquor containing 0.2 % of a commercial katalase and 40 ml/l of hydrogen peroxide 40 % by volume. The impregnated wool is subsequently left for 6 hours at room temperature and then rinsed.
The pre-treated wool is then treated with the esperase as in example 1 or 2.

A protease such as pancreatin can be used in examples 1 to 11 instead of the esperase. A wool with a soft woolly handle and shrink-resistant properties is obtained.

EXAMPLES 12 and 13

Examples 1 and 2 are repeated using, instead of 0.5 % of esperase, 0.5 % of bromelain.

Wool with a soft woolly handle and shrink resistant properties is obtained.

Examples 3 to 11 can be repeated using an appropriate amount of bromelain instead of esperase. Wool with a soft woolly handle or shrink resistant properties is obtained.

Example 14

Example 1 is repeated using, instead of esperase, 1 % of bromelain which is applied from a long bath with a liquor-to-goods ratio of 1:20. The treatment continues for 4-6 hours at 50°. After rinsing, the wool tops are dried and show a soft woolly handle and good shrink resistance

properties.

Example 15

Wool tops are pretreated as in Example 3 and after washing, further processed to finished goods. These finished goods can now be treated as in Example 14 and show excellent properties.

## Claims

1. Process for the production of wool, or protein-containing animal hair, which have a low in felt or felt-free finish defined by

   a) an area shrinkage (sum of the % shrinkage in length and the % shrinkage in width) of $\leq$ 10 % after a Cubex test of at least one hour or after 5 cycles 7 A according to IWS TM 31,

   b) a loss of yarn strength, compared with untreated wool or hair, of less than 15 % Rkm; and

   c) an elongation which deteriorates by less than 20 %,

   characterized by bringing the wool or the hair into contact with a protease and subsequently treating it at a temperature of between room temperature (20°C) and 140°C.

2. Process according to claim 1, characterised in that the protease used is esperase, pronase E, protease P, subtilysin, thermolysin, trypsin, pepsin, pancreatin or bromelain.

3. Process according to claims 1 or claim 2, characterised in that the wool or hair is impregnated with the protease, and after leaving for a short time, is treated thermally for at least 10 minutes.

4. Process according to claims 1 to 3, characterised in that the protease is used in a quantity of 0.1 to 5 %, calculated on the dry weight of the wool or hair.

5. Process according to any one of claims 1 to 4, characterised in that the wool or hair is firstly pre-treated.

6. Process according to claim 5, characterised in that the wool or hair firstly undergoes mild treatment by oxidation or reduction.

7. Wool or animal hair which is treated according to anyone of claims 1 to 6.

8. Enzymatically treated, resin free wool or animal hair with substantially unchanged scaly layer having the following properties:

   a) an area shrinkage (sum of the % shrinkage in length and the % shrinkage in width) of $\leq$ 10 % after a Cubex test of at least one hour or after 5 cycles 7 A according to IWS TM 31,

   b) a loss of yarn strength, compared with untreated wool or hair, of less than 15 % Rkm; and

   c) an elongation which deteriorates by less than 20 %.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 88/00971

**I. CLASSIFICATION OF SUBJECT MATTER** (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4]: D 06 M 16/00

**II. FIELDS SEARCHED**

**Minimum Documentation Searched** [7]

| Classification System | Classification Symbols |
|---|---|
| IPC[4] | D 06 M |

**Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched** [8]

**III. DOCUMENTS CONSIDERED TO BE RELEVANT** [9]

| Category * | Citation of Document, [11] with indication, where appropriate, of the relevant passages [12] | Relevant to Claim No. [13] |
|---|---|---|
| X | Journal of the Textile Institute, Proceedings, volume 47, 1956, A.N. Davidson et al.: "Shrink-resisting wool: some novel features and the description of a new process", pages 685-707 see page 687, no. 3; page 691, paragraph II - end -- | 1,2,4-7 |
| X | Journal of the Society of Dyers and Colorists, volume 57, 1941, W.R. Middlebrook et al.: "The application of enzymes to the production of shrinkage-resistant wool and mixture fabrics", pages 137-144 see the whole article -- | 1,2,4-7 |
| X | Textil-Praxis, volume 18, no. 3, March 1963, E.P. Frieser: "Das Filzfreiaus-rüsten von Wolle", pages 236-237 | 1,2,4-7 |

./.

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

**IV. CERTIFICATION**

| Date of the Actual Completion of the International Search | Date of Mailing of this International Search Report |
|---|---|
| 13th February 1989 | 09 MAR 1989 |
| **International Searching Authority** | **Signature of Authorized Officer** |
| EUROPEAN PATENT OFFICE | P.C.G. VAN DER PUTTEN |

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

| Category * | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No |
|---|---|---|
| | see pages 236-237, left-hand column<br>-- | |
| X | EP, A, 0134267 (KURASHIKI BOSEKI K.K.)<br>20 March 1985<br>see claims; page 3, line 16 - page 7, line 10<br>-- | 1-7 |
| A | BE, A, 536819 (WIRA)<br>13 February 1959<br>see claims | 1,2,4-7 |

---

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. EP 8800971 SA 25203

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 24/02/89
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP-A- 0134267 | 20-03-85 | | |
| BE-A- 536819 | | | |